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VI. "Notes of Researches on the Poly-Ammonias."—No. XVII.
Mixed Triammonias containing Monatomic and Diatomic
Radicals. By A. W. HOFMANN, LL.D., F.R.S. Received
July 29, 1861.

Diethylene-triamine and triethylene-triamine, a short history of which I laid before the Royal Society some weeks ago, are the first terms of a group of a series of triatomic nitrogen-bases, whose construction and composition may be varied almost ad infinitum. Similar compounds, there can be no doubt, will be produced by all the homologues of ethylene. With the exception of a few experiments on the action of ammonia on dibromide of methylene, I have not hitherto entered upon this part of the inquiry. Not less numerous is the series of triatomic bases derived from the ethylene-triamines by the further substitution of either monatomic or diatomic radicals for the remaining hydrogen-equivalents. I have satisfied myself that the ethylenated triammonias are powerfully acted upon by the iodides of methyl and ethyl, and likewise by dibromide of ethylene. I have not examined in detail the substances produced in these reactions, but I have had occasion to glance at the ethylated derivatives of the ethylene-triamines when studying the diatomic bases generated by the action of dibromide of ethylene upon the ethylated monamines.

In a former note I have pointed out that the action of dibromide of ethylene on ethylamine gives rise to the formation of

Ethylene-diethyldiamine
$$\begin{pmatrix} (C_2H_4)^{ii} \\ (C_2H_5)_2 \\ H_2 \end{pmatrix} N_2$$

and

Diethylene-diethyldiamine
$$\begin{pmatrix} C_2H_4 \end{pmatrix}_2^{ii} \\ C_2H_5 \end{pmatrix} N_2$$
.

These two compounds constitute the chief part of that portion of the volatile bases derived from ethylamine which, after several rectifications, passes over below 200°. The bases boiling above 200° are a mixture which, dissolved in hydrochloric acid, yields with dichloride of platinum a splendidly crystallized platinum-salt. By numerous crystallizations this salt may be separated into one which is difficultly soluble in water, and another which is far more soluble.

The analysis of these platinum-compounds proved them to be the salts of two bases, the formation of which in the above reaction was pointed out by theory, namely, of

$$\begin{array}{ccc} \text{Diethylene-triethyltriamine} & C_{_{10}}H_{_{25}}N_{_{3}} = \overset{\left(C_{_{2}}H_{_{4}}\right)_{_{2}}^{11}}{2} \\ C_{_{2}}H_{_{2}})_{_{3}} \end{array} \right\}N_{_{3}} \\ \text{and} \end{array}$$

$$\label{eq:Triethylene-triethyltriamine} \begin{array}{l} C_{12}H_{27}N_3 = \stackrel{\left(C_2H_4\right)_3}{\left(C_2H_5\right)_3} \\ \end{array} \right\}N_3.$$

Both these bases are oily liquids, powerfully caustic, extremely soluble in water, which boil between 220° and 250°. I have not prepared them in quantity sufficient for an accurate determination of their boiling-points. Both form neutral crystalline salts which are extremely soluble in water, and also, though less so, in alcohol.

I have established the composition of triethylated diethylene-triamine by the analysis of the chloride and bromide, which contain respectively,

$$\text{Trichloride} \quad C_{10} \, H_{28} \, N_3 \, Cl_3 = \begin{bmatrix} \left(C_2 \, H_4\right)_3^{11} \\ \left(C_2 \, H_5\right)_3^{11} \\ H_5 \end{bmatrix} \, N_3 \end{bmatrix}^{11} Cl_3,$$

and

$$\begin{aligned} \text{Tribromide} \quad C_{_{10}} \, H_{_{28}} \, N_{_3} \, Br_{_3} = \begin{bmatrix} (C_2 \, H_{_3})_2^{\ \text{ii}} \\ (C_2 \, H_{_5})_3^{\ \text{ii}} \end{bmatrix} N_{_3} \end{bmatrix}^{\text{lii}} Br_{_3}. \end{aligned}$$

I have also determined the composition of the platinum-salt and of the gold-salt. Both are well-defined beautifully crystalline compounds containing,

$$\begin{split} \text{Platinum-salt} \quad & \text{$C_{_{10}$}$ $H_{_{23}}$ $N_{_3}$ $Pt_{_3}$ $Cl_{_9}$ } = \begin{bmatrix} (\text{$C_{_2}$ $H_{_4}$})_2^{\text{ ii}} \\ (\text{$C_{_2}$ $H_{_5}$})_3^{\text{ iii}} \end{bmatrix} \text{$N_{_3}$} \end{bmatrix}^{\text{iii}} \text{$Cl_{_3}$, 3 Pt $Cl_{_2}$,} \\ \text{Gold-salt} \quad & \text{$C_{_{10}$}$ $H_{_{23}}$ $N_{_3}$ $Au_{_3}$ $Cl_{_{12}}$ } = \begin{bmatrix} (\text{$C_{_2}$ $H_{_4}$})_2^{\text{ ii}} \\ (\text{$C_{_2}$ $H_{_5}$})_3^{\text{ iii}} \end{bmatrix} \text{$N_{_3}$} \end{bmatrix}^{\text{iii}} \text{$Cl_{_3}$, 3 Au$ $Cl_{_2}$.} \end{split}$$

The simple salts of triethylated triethylene-triamine are far more soluble than those of the triamine previously mentioned. I have therefore been satisfied to establish the composition of their base by the analysis of the platinum-salt and of the gold-salt. The platinum-salt is extremely soluble in water, and crystallizes only when the solution is evaporated nearly to dryness. The analysis of these compounds

has led to the following formulæ:-

$$\begin{split} \text{Platinum-salt} \quad & \text{$\mathbf{C}_{12}\,\mathbf{H}_{32}\,\mathbf{N}_3\,\text{Pt}_3\,\text{Cl}_9 = \begin{bmatrix} (\mathbf{C}_2\,\mathbf{H}_4)_3^{\text{ii}} \\ (\mathbf{C}_2^{\text{\mathbf{H}_3}})_3^{\text{ii}} \end{bmatrix}\,\mathbf{N}_3 \end{bmatrix}^{\text{iii}}\,\mathbf{Cl}_3,\,3\,\text{PtCl}_2,} \\ \text{Gold-salt} \quad & \text{$\mathbf{C}_{12}\,\mathbf{H}_{32}\,\mathbf{N}_3\,\text{Au}_3\,\text{Cl}_{12} = \begin{bmatrix} (\mathbf{C}_2\,\mathbf{H}_4)_3^{\text{ii}} \\ (\mathbf{C}_2^{\text{\mathbf{H}_3}})_3^{\text{ii}} \end{bmatrix}\,\mathbf{N}_3 \end{bmatrix}^{\text{iii}}\,\mathbf{Cl}_3,\,3\,\text{AuCl}_3.} \end{split}$$

Whilst engaged in the study of the action of dibromide of ethylene upon ethylamine, I occasionally observed among the bases of higher boiling-points an alkaline compound remarkable for the insolubility of its chloride in alcohol. By this behaviour it was easily separated from all the other basic substances accompanying it. This base was found to be

Diethylene-diethyltriamine,
$$C_s H_{21} N_3 = \begin{pmatrix} C_2 H_4 \end{pmatrix}_2^{ii} \\ C_2 H_5 \end{pmatrix} N_3$$
.

Among the salts of this base are some of the finest compounds which have come under my notice in this inquiry.

The chloride crystallizes in leaves of the lustre of mother-of-pearl, very soluble in water, almost insoluble even in ordinary alcohol, insoluble in ether. It contains,

$$\begin{array}{ll} \text{Trichloride} & C_{s} \ H_{24} \ N_{3} \ Cl_{3} = \begin{bmatrix} (C_{2} \ H_{4})_{2}^{1i} \\ (C_{2} \ H_{5})_{2} \\ H_{6} \end{bmatrix} \ N_{3} \end{bmatrix}^{ii} Cl_{3}. \end{array}$$

The corresponding iodide is much more soluble, it was found to have the composition,

$$\begin{aligned} \text{Tri-iodide} \ \ C_8 \, H_{24} \, N_3 \, I_3 &= \begin{bmatrix} (C_2 \, H_4)_2^{\, \text{ii}} \\ (C_2 \, H_5)_2 \\ H_2 \end{bmatrix} \, N_3 \end{bmatrix}^{\text{iii}} I_3. \end{aligned}$$

To obtain this salt it is necessary to employ a great excess of hydriodic acid.

The ethylated ethylene-triamines exhibit the same tendency to form diatomic salts which I have pointed out in describing the ethylene-triamines themselves. A solution of diethylene-diethyltriamine just neutralized with hydriodic acid deposits in fact a diatomic salt,

$$C_{8} H_{23} N_{3} I_{2} = \begin{pmatrix} C_{2} H_{3} \end{pmatrix}_{2}^{\text{fi}} \\ C_{2} H_{5} \end{pmatrix} N_{3}, 2HI.$$

The finest salt of this base is the nitrate. Readily soluble in hot, and moderately soluble in cold water, it is deposited from a saturated

solution on cooling in large rectangular tables presenting the aspect of nitrate of silver. The combustion of this salt has led to the formula

Trinitrate
$$C_{8} H_{24} N_{6} O_{9} = \begin{bmatrix} (C_{2} H_{4})_{2}^{ii} \\ (C_{2} H_{5})_{2}^{i} \\ H_{6} \end{bmatrix} N_{3}^{iii} (NO_{3})_{3}$$

The formation of the diethylated diethylenetriamine is readily intelligible. I have satisfied myself that the origin of this body was always due to the presence of minute quantities of ammonia which had not been entirely removed from the ethylamine employed in the reaction.

$$3\begin{bmatrix} (C_{2} H_{5}) \\ H \end{bmatrix} N + H \\ + H \\ + H \\ + D = [(C_{2} H_{4})^{1i} Br_{2}] = \begin{bmatrix} (C_{2} H_{4})_{2}^{1i} \\ (C_{2} H_{5})_{2} \\ H_{6} \end{bmatrix} N_{3} \end{bmatrix}^{1ii} Br_{3} \\ + \begin{bmatrix} (C_{2} H_{5}) \\ H_{3} \end{bmatrix} N Br.$$

The formation of diethylene-diethyltriamine furnishes an elegant illustration of the simple mechanism involved in the construction of the polyatomic bases.

VII. "Notes of Researches on the Poly-Ammonias."—No. XVIII.

Tetrammonium-Compounds. By A. W. Hofmann, LL.D.,
F.R.S. Received July 29, 1861.

In several previous communications I have submitted to the Royal Society a sketch of the triatomic bases which are generated by the assimilation of three molecules of ammonia linked together by the intervention of diatomic molecules. In the same sketch I endeavoured to trace the general principle upon which the bases of higher atomicity are formed. I pointed out that the accumulation of ammonia-molecules is determined by the number of diatomic radicals which are fixed; that, for the production of an (n+i)-atomic ammonia, at least n diatomic radicals are required; and lastly, that the number of molecules of diatomic bromides and the quantity of ammonia involved in these accumulative processes are given in the general equation

$$n R^{ii} Br_2 + 2n H_3 N = [R_n^{ii} H_{(2n+4)} N_{(n+1)}]^{(n+i)} Br_{(n+1)} + n - 1([H_4 N]Br).$$